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Oferi Kresnawahjuesa
University of Pennsylvania

D. H. Olson
University of Pennsylvania

Raymond J. Gorte
University of Pennsylvania, gorte@seas.upenn.edu

G. H. Kühl
University of Pennsylvania

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Removal of Tetramethylammonium Cations from Zeolites

O. Kresnawahjuesa, D.H. Olson, R.J. Gorte, and G.H. Kühl*

*Department of Chemical Engineering, University of Pennsylvania, 311A Towne Building, 220 S.33rd Street,
Philadelphia, PA 10104, U.S.A.*

*Corresponding author, Fax: +1-215-573-2093; e-mail address: kuehl@seas.upenn.edu

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Abstract

Zeolite α (high-silica LTA), a potential shape-selective catalyst, is synthesized in the presence of tetramethylammonium (TMA) ions. Since TMA^+ ions are incapable of forming olefins at low temperature, temperatures in excess of 500°C are required to thermally decompose them and burn off the carbonaceous deposits, frequently causing damage to the structure. In this paper, the thermal decomposition of zeolitic TMA^+ ions is investigated. This work led to a less severe method for removing TMA^+ ions by stepwise reaction with ammonia at low temperatures. TMA^+ ions located in the supercage can easily be removed at a temperature as low as 250°C , generating mono- and dimethylamine. Sodalite cage TMA^+ ions require a temperature of not more than 400°C to be degraded. Although this treatment raises the Si/Al ratio somewhat, damage to the structure is minimal. Since the size of the zeolitic pores defines the type of molecules capable of escaping from the zeolite cavities, decomposition of TMA^+ ions in NaTMA-Y and NaTMA-high-silica sodalite have been included for comparison.

1. Introduction

Maintaining the structure of zeolites with relatively low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, e.g. 4-6, during calcination to produce the hydrogen form can be difficult because unintended steaming can cause dealumination and collapse of the structure. This is especially true for materials which are prepared using an organic template, such as a quaternary ammonium compound, because combustion of the template produces water, often in the temperature range where steaming is most severe. One can avoid some of these problems by heating first in an inert atmosphere in order to remove adsorbed water at low

temperature, followed by thermally decomposing the template at a higher temperature; finally, carbonaceous deposits built up during the decomposition can be burnt off in dry air. The decomposition of zeolitic tetrapropylammonium ions has been studied extensively; a review of the literature is given in [1]. Zeolitic alkylammonium ions containing carbon chains with two or more carbon atoms liberate olefins upon thermal decomposition leaving acid sites behind – tetrapropylammonium ions decompose in the range of 300-375°C [2] - although secondary reactions, e.g., oligomerization, may cause coke to be deposited.

Zeolite α [3], a shape-selective, small-pore zeolite of LTA topology, is synthesized using TMA⁺ ions as the template. These ions are particularly vulnerable to coking because they cannot easily form an olefin as those with longer carbon chains do, and it is critical to remove the occluded TMA without damaging the zeolite or at least keeping the damage to a minimum. Previously applied calcination procedures include conditions such as heating for 17 hours at 500°C in air [3], which appears to have resulted in a product of high crystallinity, as judged from the sorption capacities. Another method directed mainly to stabilizing the zeolite structure for catalytic purposes rather than to preserving all of the overabundant acid sites, used a complicated calcination program of first heating at a rate of 10°C/min to 550°C in moist nitrogen, then cooling to about 400°C before gradually replacing the nitrogen with air and heating again at 10°C/min to 550°C, where the sample was held for 30 min [4]. No measurements of acid site retention was reported in either of these references.

Although the initial decomposition is not expected to depend on the zeolite structure, the nature of the products leaving the pores of the zeolite depends on the size of the pores permitting egress. Therefore, as a large-pore material, zeolite Y (FAU) has been examined to determine the thermal behavior of TMA⁺ ions in the absence of restricting pores. Since the structures of zeolites Y and α contain sodalite cages, the feldspathoid high-silica sodalite (SOD), has been used to study the thermal behavior of TMA⁺ ions in a severely restricted environment, which does not permit any amine to exit.

This paper is limited to the removal of TMA⁺ ions from different zeolitic environments with emphasis on zeolite α and introduces a novel method for accomplishing this goal. While the crystallinity of the zeolitic products is reported, in addition to the determination of acid sites, detailed work dealing particularly with any changes in the zeolite structure, such as contraction of the lattice, the appearance of extra-framework-Al, and attempts to minimize these effects is in progress.

2. Experimental

Samples

Sodium zeolite Y of SiO₂/Al₂O₃ molar ratio of 5.3, Valpor CP 300-63, was obtained from PQ Corporation. It was exchanged once with TMACl (98% pure, ACROS Organics), at a pH of about 8, adjusted with TMAOH. The NaTMA-Y, in the anhydrous form, has the approximate composition, 0.77 Na₂O : 0.23 TMA₂O : Al₂O₃ : 5.3 SiO₂, as calculated from the result of the temperature-programmed ammonia/amine desorption (TPAD) and the known SiO₂/Al₂O₃ molar ratio..

Zeolite α was synthesized by a modified procedure published earlier [4,5]. The reaction mixture had the composition, 1.1 Na₂O : 2.35 TMA₂O : Al₂O₃ : 10 SiO₂ : 120 H₂O. The highly crystalline product (Fig. 1a) has the composition (equilibrated over saturated NH₄Cl solution), 0.54 Na₂O : 0.45 TMA₂O : Al₂O₃ : 5.82 SiO₂ : 4.79 H₂O. The SiO₂/Al₂O₃ ratio thus obtained is in agreement with the lattice parameter and the ²⁹Si MAS NMR spectrum. The NH₄TMA- α was prepared from the NaTMA- α by three exchanges, each for 1 h at 60°C, with 0.2N NH₄Cl, adjusted to pH 8 with NH₄OH, washing with deionized water until free of Cl⁻, and drying at ambient temperature.

High-silica sodalite was crystallized by digesting a reaction mixture of the same composition, 1.1 Na₂O : 2.35 TMA₂O : Al₂O₃ : 10 SiO₂ : 120 H₂O for a month at 95°C, using milled Ultrasil VN3SP (Degussa) as the silica source. The X-ray diffraction pattern of the product (Fig. 1b) shows no crystalline or amorphous impurity; however, microscopic examination prior to drying revealed a small amount of amorphous material. The lattice parameter was found to be 8.979Å, in excellent agreement with 8.975Å reported by Baerlocher and Meier [6] for SiO₂/Al₂O₃ = 10.6. The material has the approximate composition (calculated from the TPAD result and assuming a SiO₂/Al₂O₃ molar ratio of 10), 0.26 Na₂O : 0.74 TMA₂O : Al₂O₃ : 10 SiO₂.

Methods

A combination of thermogravimetric analysis (TGA) and temperature-programmed amine/ammonia desorption (TPAD), based on a method described by Kerr and Chester

[7], with a heating rate of 10°C/min was used to determine the temperatures and quantities of base desorption and weight loss in helium flowing at 100 cm³/min. In separate experiments *in vacuo* at a heating rate of 10°C/min, the desorbed products were identified by mass spectrometry using a Transpector Gas Analysis System. The apparatus had a limit of about 500°C.

The treatment of the samples with gaseous ammonia was carried out in a quartz reactor at constant temperature. After having been placed in the reactor, the samples were pre-dried *in vacuo* at a temperature rising to 100°C and then heated to the desired temperature in flowing helium, 60 cm³/min. While the helium stream was by passing the reactor, ammonia, 6 cm³/min, was added; the gas mixture was sampled to make sure that the gas composition remained constant. After 1000 sec, the gas mixture was directed over the sample. The effluent gas was analyzed by gas chromatography using an Alltech Haysep Q 80/100, 6'x1/8" column, ser.# 722-4713. The column temperature was 90°C, and that of the detector was 100°C, the He carrier gas flow rate was 25 cm³/min. The gas samples were taken at the times indicated in the figures. Scale-up experiments were conducted in a tube furnace with nitrogen instead of helium.

3. Results

The results of the TGA/TPAD determinations are shown in Figures 2a-d and summarized in Table 1. NaTMA-sodalite (Fig. 2a) loses base in one rapid step centered at 600°C, whereas the base desorption from NaTMA-Y (Fig. 2b) occurs at a much lower temperature, 480°C. Base is released from NaTMA- α (Fig. 2c) at different rates in two

successive steps, the first in the range of 300-465°C, followed by a higher rate elimination of base centered at 500°C. None of the three TGA curves exhibit a distinct dehydroxylation step. After removal of the sodium by exchange with ammonium ions, zeolite α yields a bimodal curve consisting of a relatively slow release of base up to 400°C, followed by a rapid base elution centered at 500°C, and the TGA curve exhibits a dehydroxylation step centered at about 700°C (Fig.2d). The mass spectra of the gaseous products obtained by heating samples of zeolites Y and α in vacuum are shown in Fig. 3a-c. In all three figures, water, ammonia, amines, and olefins are released above 325°C. Particularly noteworthy is the appearance of water in this temperature range for all three samples, and of mono- and dimethylamine at low temperature from $\text{NH}_4\text{TMA-}\alpha$, as well as the again ascending ammonia curve in the mass spectrum of $\text{NaTMA-}\alpha$ after its desorption had reached a maximum (Fig.3b).

The gaseous products generated by ammonia treatment at constant temperature were analyzed by gas chromatography as a function of time, Figures 4a(NaTMA-Y at 300°C), 4b($\text{Na,TMA-}\alpha$ at 250°C), and 4c($\text{NH}_4\text{TMA-}\alpha$ at 250°C). In contrast to high-silica sodalite, where no product was observed, the same treatment of NaTMA-Y at 300°C yields mono-, -di-, and trimethylamines (Fig. 4a). The products of the zeolite α samples consist of only mono- and dimethylamine indicating that the pore size of this zeolite does not permit trimethylamine to pass at 250°C.

The TGA/TPAD diagram of $\text{NH}_4\text{TMA-}\alpha$ treated for 2 h with ammonia at 250°C indicates that the reaction of TMA^+ with ammonia was incomplete, but an additional 2-h treatment yielded essentially the same curves (Fig.5a). The results suggest that either

some of the TMA^+ ions do not react with NH_3 at this temperature or the products obtained cannot exit. Logically, this nitrogenous material must be located in the sodalite cages, and a calculation reveals that there are 2 N per unit cell, i.e., 2 N/sodalite cage. When treated with ammonia at 400°C for 4h, the second step essentially disappeared indicating that this nitrogenous material was removed (Fig.5b).

4. Discussion

A. Calcination in Inert Atmosphere

Na,TMA-high-silica Sodalite

Although not considered a zeolite, but rather a feldspathoid, sodalite consists of the same cages that occur as β -cages in zeolites Y and α . The 6-ring openings are estimated to be only about 0.26 nm in diameter, and are expected to be impenetrable to most hydrocarbons, as well as all amines. Baerlocher and Meier [6] observed that each sodalite cage of their Na-free preparation contains one TMA^+ and that the methyl groups are H-bonded to framework-O with CH--O distances of only 0.306 nm.

The TPAD/TGA curves (Fig. 2a) show a slight release of base below 450°C . The base observed is probably due to amines formed by hydrolysis during the crystallization and liberated from the amorphous impurity and/or from surface sites, since this material has extremely small crystallite size. The weight loss at low temperatures is largely due to dehydration. The bulk of the base is liberated in one giant step over the temperature range $480\text{-}700^\circ\text{C}$.

At 482°C, the weight was 76.2 mg/g of ash higher than the final weight at 710°C, and the base release was 0.099 meq/g, compared with 1.863 meq/g at 710°C. Therefore, the base liberated above 482°C was 1.764 meq/g, or 30.0 mg NH₃/g, leaving 46.2 mg of a non-basic compound eliminated from the sodalite in this step, per gram. Ethene (kinetic diameter $\sigma = 0.39$ nm [9]) and even methane ($\sigma = 0.38$ nm) cannot penetrate the 6-member rings, whereas ammonia ($\sigma = 0.26$ nm) and water ($\sigma = 0.265$ nm) can. The hydrocarbon with the smallest kinetic diameter is acetylene ($\sigma = 0.33$ nm), and the release of one molecule of acetylene per molecule of ammonia gives a weight loss of 75.9 mg for ammonia plus acetylene per gram, in agreement with the observation. Indeed, heating of NaTMA-sodalite *in vacuo* and analyzing the liberated gas by mass spectrometry produced a strong peak of $m/e = 26$ in the range of 550-670°C.

The initial reaction can then be represented by the equation,

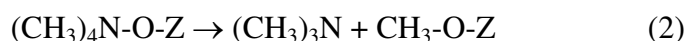


Methane is trapped within the sodalite cages and is eventually, at higher temperature, thermally decomposed to form coke, which is evident from the dark color of the TGA residue, and hydrogen, but no additional acetylene is desorbed at temperatures from 670 to 800°C. However, this scenario does not take into account that the decomposition of CH₃OZ should generate water (see below), one half mol/mol of ammonia, which can escape from the sodalite cages. The weight loss observed does not accommodate this water. It seems likely that the water formed hydrolyzes framework-Al and generates

hydroxylated Al species, which are then dehydrated at high temperature, and the water thus released is included in the weight loss above 670°C. Indeed, the X-ray diffraction pattern of NaTMA-sodalite heated in flowing nitrogen at 10°C/min to 600°C and held at this temperature for 4 hours shows a 60% reduction of crystallinity and a contracted lattice with a unit cell parameter of 8.886 Å compared with 8.979 Å for the parent.

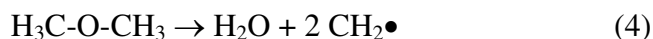
NaTMA-Y

The TPAD/TGA for NaTMA-Y (Fig. 2b) shows a main step centered at about 480°C, about 120° lower than observed for NaTMA-sodalite. The lower temperature is attributable to the open structure, which permits decomposition products to diffuse out more easily. The base concentration is 0.939 meq/g, based on final weight, corresponding to a weight of 15.96 mg NH₃, 29.11 mg CH₃NH₂, 42.26 mg (CH₃)₂NH, or 55.4 mg of (CH₃)₃N. The observed weight loss in the range of 360-540°C is about 55 mg (the minor slow release of base above 540°C is believed to be an artifact possibly caused by temporary adsorption in the lines and is included in the total meq/g). The initial reaction may then be represented by:



Since the TMA⁺ ion was introduced by ion exchange, there is no doubt that all TMA was located in the supercages. However, agreement of the weight loss with the weight of trimethylamine calculated from the base titrated does not prove that the product actually leaving the zeolite is trimethylamine, as secondary reactions, like those observed by Wu

et al [8] can occur. Indeed, the mass spectrum (Fig. 3a) indicates that the reaction begins with release of ammonia at 325°C, followed closely by the appearance of methylamine, while di- and trimethylamines are desorbed at a lower concentration. All base curves reach their maxima at about 480°C, in agreement with the TPAD (Fig. 2b), shortly after olefin desorption begins to increase rapidly. There is only a minor release of olefins up to about 440°C, while mostly oligomers appear to be formed. The curves corresponding to $m/e=28$ (ethene) and $m/e=41$, which is believed to represent mainly propene and butene, increase sharply at about 440°C, and are still ascending at 490°C, although they must peak shortly thereafter, as the TGA (Fig.2b) suggests. The steep rise of these curves is believed to be mainly due to depolymerization of oligomers, but may contain contributions due to thermal decomposition of residual amines. Water is lost during the entire range above about 350°C (the peaks of $m/e=17$ and 18 below 325°C are entirely due to water). The loss of water in this temperature range must involve framework oxygen. Ammonia has been reported to induce dehydroxylation at reduced temperature [10]. However, as will be shown below, the water loss we observed in this temperature range is derived from TMA sites only. It is, therefore, proposed that the loss of water is caused by demethoxylation and immediate decomposition of the dimethylether formed,



Regardless of whether the composition of the effluent is $(\text{CH}_3)_3\text{N} + 0.5\text{C}_2\text{H}_4 + 0.5\text{H}_2\text{O}$ or $(\text{CH}_3)_2\text{NH} + \text{C}_2\text{H}_4 + 0.5\text{H}_2\text{O}$ or $\text{CH}_3\text{NH}_2 + \text{C}_3\text{H}_6 + 0.5\text{H}_2\text{O}$ or even $\text{NH}_3 + \text{C}_4\text{H}_8 + 0.5\text{H}_2\text{O}$, the weight loss is calculated to be $0.939 \times 82 = 77$ mg/g of final weight, in excess of what has been observed. The discrepancy may be due to the final weight having been measured at a low 750°C ; an additional weight loss of 23 mg would increase the base to 0.96 meq/g and the calculated weight loss to 78.7 mg, in agreement with the then measured 78 mg/g.

Whereas our data show no loss of base at temperatures below 360°C , the previously cited earlier publication [8] indicates that trimethylamine, as well as other compounds, are eliminated upon extended heating at 275°C . The discrepancy may be attributable to the long, 3-h heating period at this temperature for sample collection in the earlier work. A minor release of dimethylamine observed at low temperature in the mass spectrum (Fig. 3a) after heating in vacuum is believed to derive from an impurity in the TMACl used for ion exchange.

Na,TMA- α

The TPAD/TGA curves of zeolite NaTMA- α (Fig.2c) show a bimodal loss of base and weight in the range of $300\text{-}465$ and $465\text{-}540^\circ\text{C}$, which is more clearly recognized in the derivative curve (not shown). However, because of the overlap of the two types of reactions identified above, it is more convenient to divide the TMA^+ into those ions located in the supercages and those in the sodalite cages. The reactions are expected to be similar to those observed for zeolite Y and sodalite, respectively. Including the water

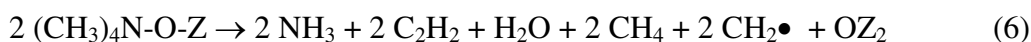
of hydration, the total weight loss is about 300 mg/g of final weight at 980°C, and the total amount of base liberated is 1.693 meq/g of final weight.

After the water desorption, the first step from 300-465°C corresponds to about 0.55 meq of base/g and a weight loss of about 45 mg/g of final wt. Regardless of whether the composition of the effluent is $(\text{CH}_3)_3\text{N} + 0.5\text{C}_2\text{H}_4 + 0.5\text{H}_2\text{O}$ or $(\text{CH}_3)_2\text{NH} + \text{C}_2\text{H}_4 + 0.5\text{H}_2\text{O}$ or $\text{CH}_3\text{NH}_2 + \text{C}_3\text{H}_6 + 0.5\text{H}_2\text{O}$ or even $\text{NH}_3 + \text{C}_4\text{H}_8 + 0.5\text{H}_2\text{O}$, the weight loss is calculated to be $0.55 \times 82 = 45.1$ mg/g of final weight, in agreement with the observation. Again, no dehydroxylation step is observed in the TGA curve (Fig.2c), so that the reactions in the first step are most likely similar to those observed with NaTMA-Y.

Also similar to NaTMA-Y, the mass spectrum shows that the decomposition reaction begins with desorption of water at about 340°C, closely followed by release of ammonia, tri- and monomethylamines, all reaching a maximum in the range of 430 -450°C, while dimethylamine has again the lowest concentration, but does not peak by 480°C (Fig. 3b). Desorption of trimethylamine from zeolite α was unexpected, but it was found earlier [11] that isopropylamine, which is of similar size, was slowly adsorbed by a high-silica LTA zeolite above about 150°C. The kinetic diameter σ [9] of isobutene, also of similar size, is 0.50 nm, and it is not surprising that trimethylamine can exit through the 8-member rings at elevated temperature. The earlier increase in the rate of olefin desorption compared to zeolite Y, along with the slower maximal rate, suggests that either more olefins are desorbed before they can oligomerize or that the oligomers begin to decompose at a lower temperature. Significantly, after having reached a maximum,

the ammonia curve increases again beginning at about 460°C, while the water desorption continues to decline. This increased ammonia release signals the beginning decomposition of the TMA⁺ ions located in the sodalite cages.

The decomposition of the sodalite-cage TMA⁺ ions is expected to be the same as in sodalite, i.e., resulting in desorption of ammonia and acetylene, while water generated by demethoxylation may or may not be desorbed (the mass spectrum shows that water desorption does not increase with the ammonia release). In contrast to sodalite, where acetylene has to migrate through many 6-member rings in order to escape into the gas phase, any acetylene formed within the sodalite cages of the LTA topology needs to pass through only one 6-member ring to arrive in the supercage. From here it can easily exit the crystal via 8-ring openings, thus explaining the lower temperature of this steep part of the TPD curve, 500°C, compared with that of sodalite, 600°C. The net reaction is then,



One TMA⁺/sodalite cage amounts to 0.66 meq/g. Assuming that ammonia and acetylene are desorbed from the sodalite cages, the weight loss would be 28.4 mg. The remaining 1.033 meq/g are then residing in the supercages and are expected to decompose according to Eq.(2)-(5) for a weight loss of 84.7 mg. The total weight loss between 350 and 550°C should be about 113 mg, compared with about 105 mg found. However, acetylene is likely to be released more slowly in this temperature range. If only ammonia is desorbed, then the expected weight loss is 11.2 mg/g and the theoretical total would be 95.9 mg/g.

In addition to acetylene, further desorption above 550°C is expected to include products from consolidation of coke and thermal decomposition of methane (possibly generating more acetylene), and water from dehydration of hydroxylated Al.

The minor low-temperature methylamine desorption is attributed to hydrolysis, during crystallization, of the impurity observed in zeolite Y, assuming that the TMAOH used as starting material was prepared from the TMACl containing this impurity.

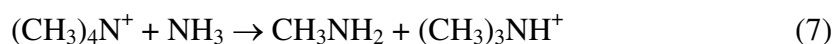
NH₄TMA- α

All sodium ions are exchangeable with ammonium ions in the presence of TMA; the Na⁺ and NH₄⁺ ions are located in the supercage. The TPA/TGA curves are shown in Figure 2d. As expected, a bimodal release of base is observed. In the first step, about 2.15 meq/g of final wt., corresponding to 36.6 mg of ammonia/g, is released, compared to the actual weight loss of about 41.8 mg/g, which includes residual water from the overlap of water and ammonia desorption. The mass spectrum (Fig.3c) shows, simultaneously with the desorption of ammonia, releases of mono- and dimethylamines, while ammonia is generated up to 350°C. Other than a trace amount of methylamine attributed to an impurity, this low-temperature release of amines was not observed in the mass spectrum of NaTMA- α suggesting that these amines are generated by reaction of TMA⁺ ions with ammonia. This reaction opens a path for degrading such ions by reaction with gaseous ammonia forming smaller amines that can easily migrate out of the pores. The appearance of amines at this temperature also indicates that not the entire base release represents ammonia, but includes these amines, which raises the estimated weight loss

closer to the value measured. The loss of base calculated from the composition of the zeolite was expected to be 2.39 meq/g; the deficiency of 0.24 meq/g has apparently reacted with TMA⁺ ions located in the sodalite cages forming additional amine that has not desorbed.

In the second step ranging from 400-550°C, 2.25 meq of base/g of final weight was observed, although the loss of base calculated from the composition was expected to be 2.01 meq/g. The excess base is identical to the base missing in the first step. .

This second step in the TPA/TGA curves represents the combination of TMA⁺ ions in both supercages and sodalite cages. The TMA⁺ ion believed to be located in the sodalite cage corresponds to 0.72 meq/g; to this number has to be added the ammonia that appears to have formed additional amines by reacting with sodalite cage TMA⁺ according to



for a total base in the sodalite cages of 0.96 meq/g. The TMA⁺ initially located in the supercages amounts to $2.01 - 0.72 = 1.29$ meq/g.

While the decomposition of TMA⁺ in the different locations cannot be discerned in the TPA/TGA determination, the mass spectrum (Fig.3c) shows that mono-, di-, and trimethylamine, as well as water, desorptions reach their maxima at about 440-460°C, similar to the results from NaTMA- α . Also, ethene and propene are desorbed in a pattern

similar to that observed with NaTMA- α . The high-temperature ammonia elution begins at about 375°C and initially rises rather slowly, compared with NaTMA- α ; then, without reaching a maximum, the curve ascends rapidly from 425°C on, while the water desorption decreases. This feature is attributed to the decomposition of sodalite cage TMA⁺ ions and their products from reaction with ammonia.

In contrast to the findings on NaTMA-Y and NaTMA- α , the TGA curve of NH₄TMA- α (Fig.2d) contains a dehydroxylation step at about 700°C. This loss of water is equivalent to the ammonium ions, 0.5 H₂O/NH₃, indicating again that the thermal decomposition of TMA⁺ ions does not generate acid sites.

B. Treatment with Ammonia at Elevated Temperatures

NaTMA-high-silica Sodalite

Treatment of this material with gaseous ammonia at 250°C yields only a trace amount of monomethylamine immediately upon contact with ammonia. Since the pore size is insufficient to permit any amines generated to exit the sodalite cages, this very minor reaction is attributed to TMA⁺ ions located on surface sites of the small crystallites and, possibly, in the amorphous impurity.

NaTMA-Y

The GC analysis of the effluent gas obtained by treating 1.15g of NaTMA-Y with ammonia at 300°C is shown in Fig.4a. It is apparent that ammonia reacts with the TMA⁺ ions immediately upon contact with the zeolite. Integration of the curves and

normalization to the weight based on ash indicates that 451 μmol of methyl-, 783 μmol of dimethyl-, and 598 μmol of trimethylamine per gram were eluted. Since the reaction of one mol of TMA^+ with ammonia produces either four mol of CH_3NH_2 , two mol of $(\text{CH}_3)_2\text{NH}$, or four thirds of a mol of $(\text{CH}_3)_3\text{N}$, these numbers correspond to a total of 953 μmol of TMA^+ /g, based on ash, in agreement with the 939 μmol found by TPAD (Fig. 2a); the latter number may be corrected for the coke present in the final weight of the TGA, raising it insignificantly to about 0.950 meq/g. The normalized ammonia consumption amounts to 1294 $\mu\text{mol/g}$ of ash, whereas the quantity expected to be consumed in order to generate the products indicated is 880 μmol of ammonia/g of ash. The ammonia-free gas phase in the reactor at the beginning of the reaction appears as an ammonia consumption of about 45 $\mu\text{mol/g}$ and needs to be deducted from the ammonia consumption. The difference of 369 $\mu\text{mol/g}$ of ash is insufficient to retain all acid sites generated in the ammonium form, but a considerable percentage of ammonium ions is expected to exist at this temperature in equilibrium with the gas phase containing about 70 Torr of NH_3 .

NaTMA- α .

Treatment of 0.44g of this material with ammonia at 250°C is shown in Fig.4b. The GC curves, after integration and normalization to the weight based on ash, indicate that 282 μmol of methylamine and 3273 μmol of dimethylamine/g of ash were eluted, corresponding to 1707 μmol of TMA/g of ash, in agreement with the TPAD result, 1693 $\mu\text{mol/g}$ (Fig. 2c). Ammonia consumed amounts to 4080 $\mu\text{mol/g}$ of ash, while the products formed require only 1848 μmol of ammonia/g of ash. The conversion of the

cationic sites to the ammonium form requires 1707 μmol of ammonia/g of ash, and about 45 μmol NH_3 needs to be deducted for the false ammonia consumption caused by the ammonia-free gas volume in the reactor. This leaves 480 μmol NH_3/g , which may be interpreted as a minor physisorption of ammonia amounting to only 8 mg/g of ash.

NH₄TMA- α

The ammonium-exchanged form, 0.45g, was treated with ammonia at 250°C (Fig.4c). After integration and normalization, the GC curves indicate that 1934 μmol of monomethylamine and 817 μmol of dimethylamine/g of ash were eluted, corresponding to 892 μmol of TMA/g of ash. A quantity of 3057 μmol of ammonia/g of ash was consumed, while the products require only 1859 μmol NH_3/g of ash. The conversion of the TMA^+ to NH_4 sites requires 892 $\mu\text{mol}/\text{g}$ of ash, and about 45 $\mu\text{mol}/\text{g}$ of ash has to be deducted for the dead volume of the reactor, leaving an excess of ammonia consumed of 261 $\mu\text{mol}/\text{g}$ of ash which would amount to 4.4 mg of ammonia/g of ash. However, these numbers are not meaningful because a major portion of the original NH_4^+ ions decomposed during the preheat period, and some of the ammonia produced reacted with TMA^+ ions, so that the ammonia consumption measured by GC does not properly represent the ammonia consumed by the reaction with TMA^+ ions. Also, the amines produced by reaction with ammonia generated by decomposition of ammonium ions, and desorbed during the heat-up and preheat periods were not measured by GC. The TMA^+ calculated from the amines measured by GC is only about 60% of the quantity expected.

The same $\text{NH}_4\text{TMA-}\alpha$ was treated with ammonia at 250°C in a scale-up experiment.

TPAD examination of a sample taken after 2 hours indicated that the reaction with ammonia was incomplete. However, 4 hours of treatment yielded an essentially identical TPAD curve (the sample was pre-dried at 100°C , Fig.5a). The TGA/TPAD shows:

Step 1: from $160\text{-}460^\circ\text{C}$: 2.75meq of base/g corresponding to 46.75 mg NH_3 (~45 mg observed)

Step 2: from 460°C -end: 1.33meq of base/g corresponding to 40 mg $\text{NH}_3+0.5\text{C}_2\text{H}_2$ (40 mg observed)

Step 3: from $670\text{-}760^\circ\text{C}$: weight loss of 25 mg observed; dehydroxylation expected: 24.8 mg

All TMA^+ ions located in the supercages must have reacted with ammonia in step 1, because no significant further reaction occurred after the 2-hour treatment at 250°C . The nitrogenous material apparently left unreacted, 1.33meq/g, amounts to about 2 N/u.c., based on the known 6.14 Al/u.c. Since these two nitrogen moieties did not react while the others did, it is likely that they are located in the sodalite cages. However, a sodalite cage can accommodate only one TMA^+ ion [6]; therefore, it is likely that the sodalite-cage TMA^+ has reacted with ammonia according to Eq.(7). The methylamine generated is a stronger base ($\text{pK}_b=3.37$) than trimethylamine ($\text{pK}_b=4.20$)[12] and probably changes places with the latter, leaving methylammonium ion and trimethylamine as products. Neither amine can escape through the 6-membered rings. Because of space limitations, the trimethylamine cannot be degraded further by reaction with ammonia. The residue of the TPAD/TGA determination generated in step 2 contains carbonaceous deposits that result in a weight loss of 17.8 mg/g of final weight, as determined by burning in air.

When the ammonia treatment was carried out for 4 h at 400°C, the nitrogenous material located in the sodalite cages was removed as well, as the TPA/TGA of the product shows (Fig. 5b). Any ammonium ions eventually replacing the TMA⁺ ions are expected to be located in their proper positions in the supercages. There appears to be a normal decomposition of ammonium ions up to about 435°C amounting to about 4.1 meq/g, but the expected weight loss of 68 mg/g does not agree with the observed value, 102 mg/g, and it seems that the discrepancy is too large to be attributable to adsorbed water. Closer inspection reveals slight inflections in the TPA curve at about 260°C (~2.1 meq/g) and 435°C (~4.1 meq/g).

The slight change in the slope of the titration curve between 435 and 550°C is probably due to thermal decomposition of a small quantity of methylammonium ions retained within the sodalite cages. The loss of base above 435°C is about 0.55 meq/g, while the weight loss is about 20 mg/g. These numbers suggest that ammonia and acetylene are lost in the ratio of 2:1. When an ammonia-treated (250°C) sample was subjected to ammonia treatment at 400°C, gradual loss of acetylene was observed by GC indicating that the proposed reaction does occur.

The zeolite structure remains unaffected by ammonia treatment at 250 and 300°C. The reaction of ammonia with sodalite cage TMA at 400°C is accompanied by loss of water, probably by ammonia-induced dehydroxylation [10]. The result is a contraction of the

lattice, i.e., an increase in the framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio to values between 7 and 8 and a slight decrease in crystallinity, up to 10% after 4 h at 400°C.

A sample of the 4-h at 250°C ammonia-treated $\text{NH}_4\text{TMA-}\alpha$ was subjected to a 4-h ammonia treatment at 400°C. The mass spectrum of the products obtained upon temperature-programmed heating of this material *in vacuo* shows low-temperature methylamine desorption of considerably higher intensity than observed for untreated $\text{NH}_4\text{TMA-}\alpha$, in addition to release of ammonia. This information explains the weight loss found on the 400°C ammonia-treated $\text{NH}_4\text{TMA-}\alpha$ (see above): 2 meq/g of NH_3 plus 2.1 meq/g of CH_3NH_2 totals 99 mg/g, in good agreement with the 102 mg/g found. Since the supercages of the 250°C ammonia-treated $\text{NH}_4\text{TMA-}\alpha$ contained only ammonium ions, the question arises, how methylamine can be desorbed at low temperature after ammonia treatment at 400°C. As mentioned above, the treated zeolite is in the dehydroxylated form, i.e., some aluminum has been removed from the framework [13]. Such a reaction would open a 6-membered ring, perhaps sufficiently to permit methylamine to pass and be desorbed, while trimethylamine is thermally degraded. The small quantities of ammonia and acetylene released above 435°C are likely to be generated by thermal decomposition of methylammonium ions in undamaged sodalite cages.

Conclusion

We have shown that TMA^+ ions can be removed from zeolite α at lower temperatures than customary. The zeolite structure remains unaffected when the TMA^+ ions located in the supercages are degraded by reaction with ammonia at 250°C and replaced with NH_4^+

or CH_3NH_2^+ ions, while methyl- and dimethylamines are removed. Although sodalite cage TMA^+ ions also react, the reaction products, trimethylamine and methylammonium ions, are locked in, but their thermal decomposition products, ammonia and acetylene, are desorbed above 460°C in an inert gas stream.

The ammonia treatment, when carried out at 400°C , is accompanied by loss of water, probably by ammonia-induced dehydroxylation. This reaction results in a contraction of the lattice, i.e., an increase in the framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio to values between 7 and 8 and a slight decrease in crystallinity, up to 10% after 4 h at 400°C . Further work is in progress to determine whether this hydrolysis can be avoided.

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Legends for Figures

Figure 1. X-ray diffraction patterns of

- a) zeolite α ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.8$).
- b) high-silica sodalite ($\text{SiO}_2/\text{Al}_2\text{O}_3 \approx 10$)

Figure 2. TGA/TPAD at $10^\circ/\text{min}$ in flowing helium, 100 cc/min. \square : TPAD; \circ : TGA

- a) Na,TMA-sodalite ($\text{SiO}_2/\text{Al}_2\text{O}_3 \approx 10$)
- b) Na,TMA-Y ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.3$)
- c) NaTMA- α ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.8$)
- d) NH_4 TMA- α ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.8$)

Figure 3. TGA/Mass spectrum of products desorbed by heating at $10^\circ/\text{min}$ in vacuum
top: TGA, bottom: mass spectrum

- a) NaTMA-Y ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.3$)
- b) NaTMA- α ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.8$)
- c) NH_4 TMA- α ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.8$)

Figure 4. Gas chromatogram of products from ammonia treatment

- \circ NH_3 ; \blacktriangle CH_3NH_2 ; Δ $(\text{CH}_3)_2\text{NH}$; \blacksquare $(\text{CH}_3)_3\text{N}$
- a) NaTMA-Y ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.3$) at 300°C
- b) NaTMA- α ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.8$) at 250°C
- c) NH_4 TMA- α ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.8$) at 250°C

Figure 5. TGA/TPAD (at $10^\circ/\text{min}$ in flowing helium, 100 cc/min) of ammonia-treated NH_4 TMA- α ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.8$). \square : TPAD; \circ : TGA

- a) treated with ammonia for 4 h at 250°C
- b) treated with ammonia for 4 h at 400°C

| Zeolite | Decomposition of Ammonium Ions | | | Decomposition of Tetramethylammonium Ions | | |
|-------------------------------|--------------------------------|-------------|----------------|---|-------------|----------------|
| | Range, °C | Base, meq/g | Wt. Loss, mg/g | Range, °C | Base, meq/g | Wt. Loss, mg/g |
| NaTMA-Sodalite | | | | 480-760 | 1.764 | 76.2 |
| NaTMA-Y | | | | 360-540 | 0.939 | 55 |
| NaTMA- α | | | | 300-465 | 0.55 | 45 |
| | | | | 465-540 | 1.143 | 60 |
| NH ₄ TMA- α | 140-400 | 2.15 | 41.8 | 400-550 | 2.25 | 94.6 |

Table 1. Summary of TPAD/TGA data

Figure 1

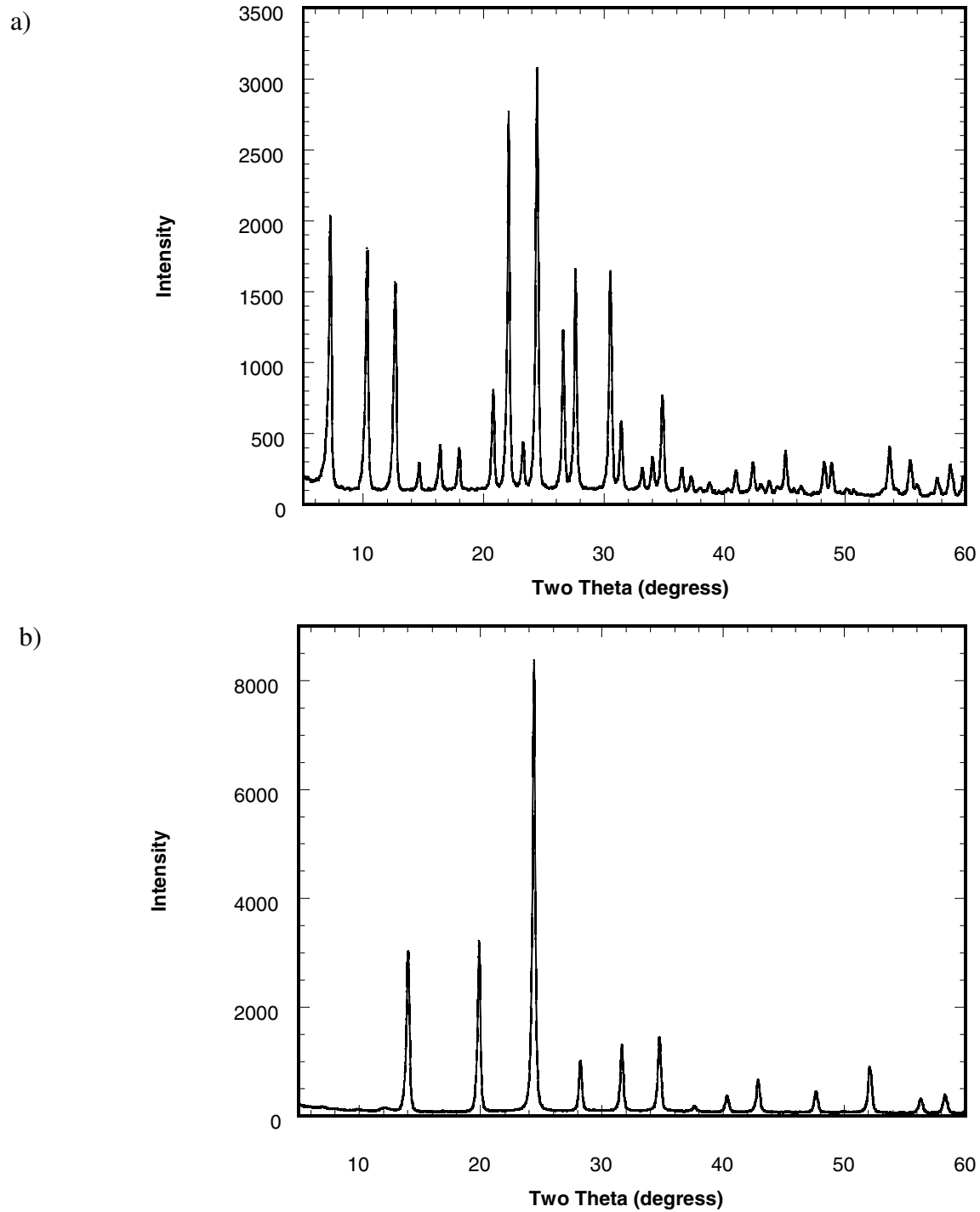


Figure 2

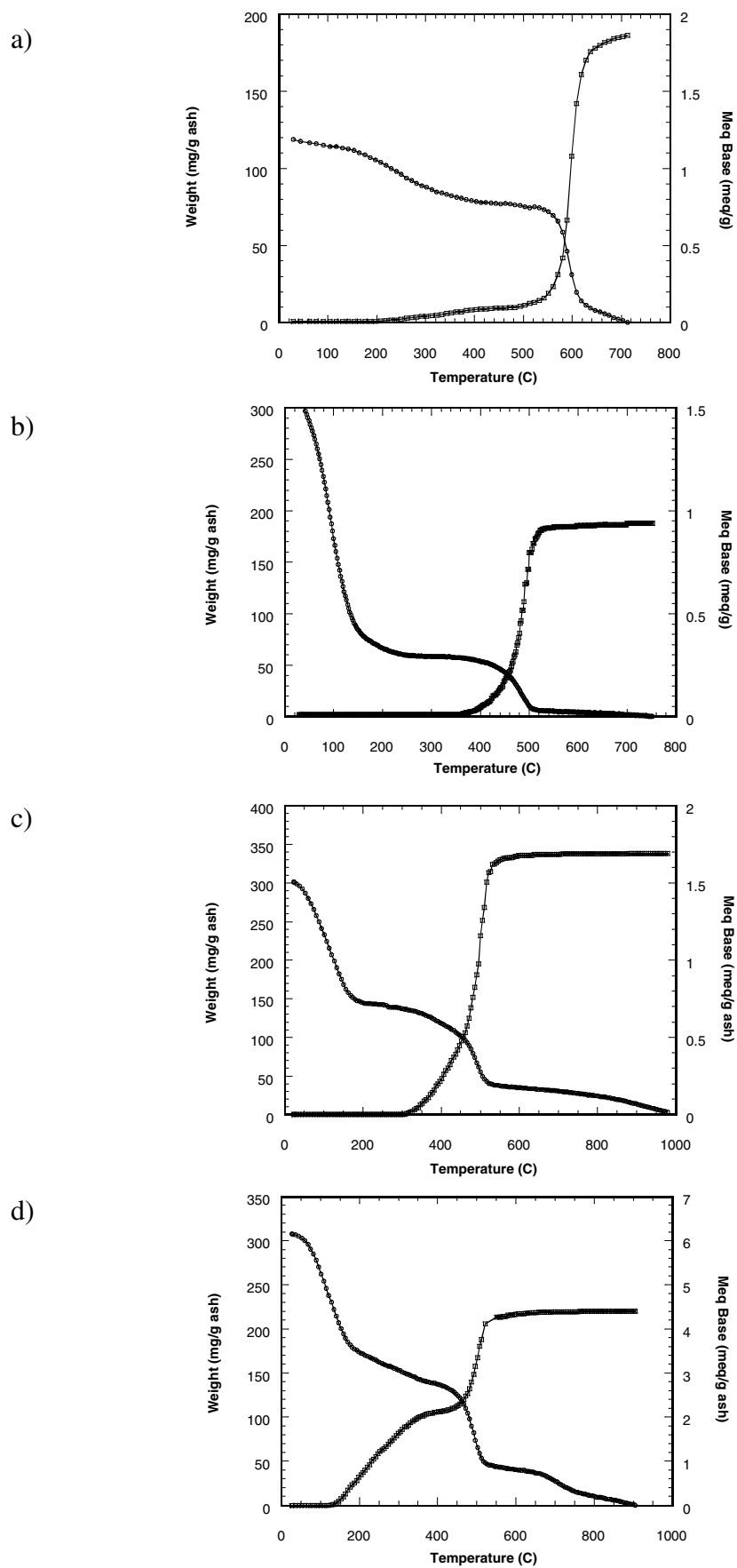


Figure 3

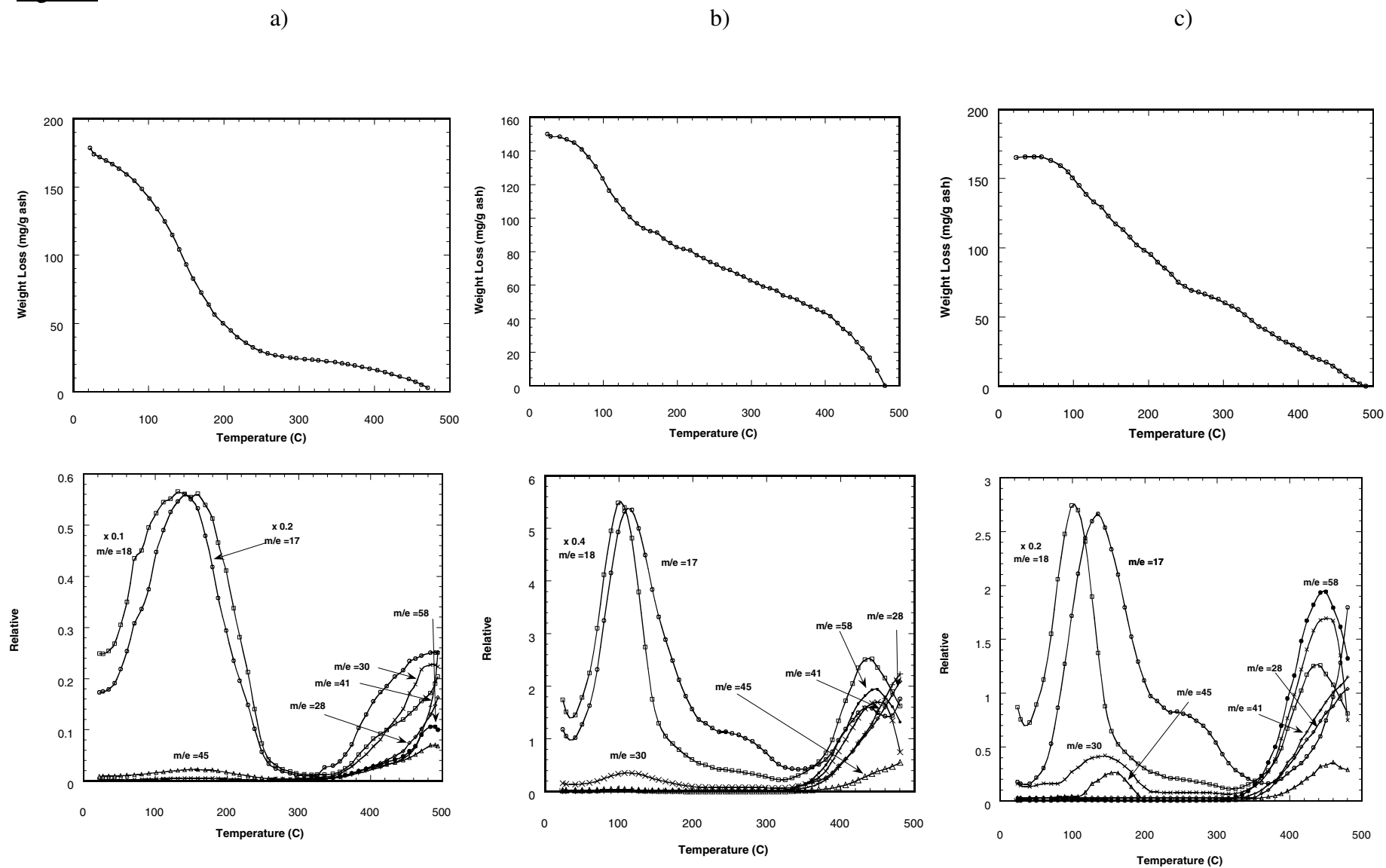


Figure 4

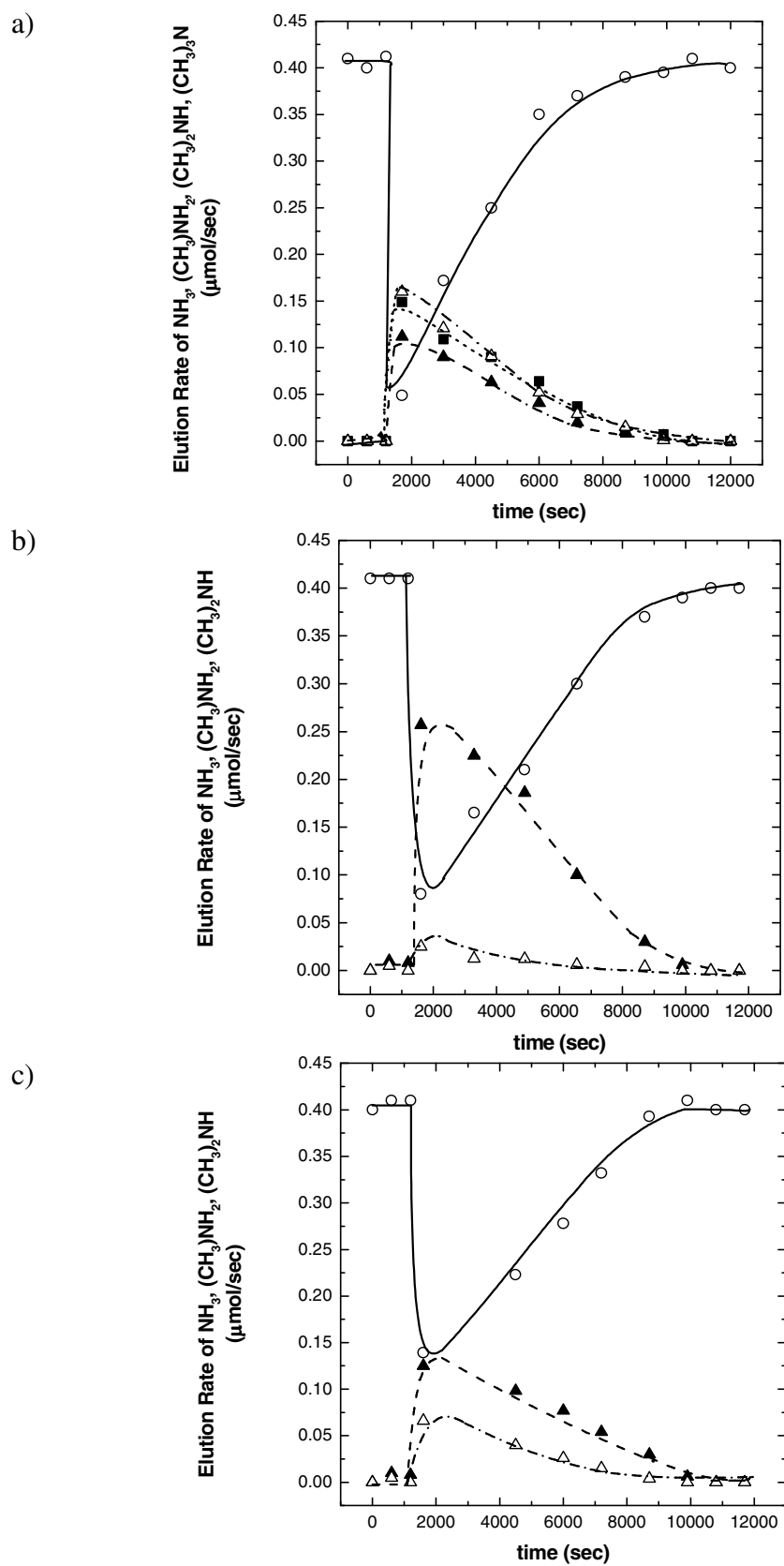


Figure 5

